20

1

# PROCESSES AND SYSTEMS FOR THE PRODUCTION OF PROPYLENE GLYCOL FROM GLYCEROL

## ACKNOWLEDGMENT OF GOVERNMENT SUPPORT

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#### **FIELD**

This disclosure relates to processes and systems for the <sup>15</sup> conversion of glycerol to propylene glycol, including processes that recycle the propylene glycol product stream to serve as a solvent for the glycerol feed stream.

#### BACKGROUND

It is known to convert glycerol to propylene glycol. Glycerol that is derived from a bio-diesel process has to be treated in a number of steps prior to its conversion to propylene glycol. For instance, one step includes the acidification of the 25 glycerol feed to decant the free fatty acids. In addition, the glycerol is often thermally stripped to remove methanol. Thermally stripping the glycerol feed to remove methanol, however, has the adverse consequence of removing much of the water that is otherwise necessary to enable the catalytic 30 process. Thus, concentrated glycerol feed must be diluted with water to about 40% to 60% by weight prior to its use as reactor feed. However, the necessary addition of water to the feed stream places a burden on the overall system since it must later be removed in downstream distillation separation 35 processes. As such, having to remove water that was just added in previous steps is energy inefficient, and increases production time and the overall cost of the process.

Further, once the concentrated glycerol is diluted with water, a base reagent (such as sodium hydroxide) must be 40 added to the glycerol before it can be used as reactor feed. Unfortunately, the base reagent that leaves with the reactor product is not easily recycled and is wasted during the recovery process. Finally, there is significant data on this process that suggests that in many cases the process operates near a 45 hydrogen mass transport limited regime.

Accordingly, there exists a need for improved processes to convert glycerol to propylene glycol.

### SUMMARY

Processes and systems for converting glycerol to propylene glycol are disclosed. The glycerol feed is diluted with propylene glycol as the primary solvent, rather than water which is typically used. The use of water as a solvent is disadvantageous since, among other things, it must later be removed by downstream separation processes. The diluted glycerol feed is sent to a reactor (such as a trickle-bed reactor) where the glycerol is converted to propylene glycol (as well as other byproducts) in the presence of a catalyst. The propylene glycol-containing product from the reactor is recycled back as a solvent for the glycerol feed. In certain embodiments, the amount of water in the recycle solvent stream is less than about 20% by weight, and the diluted glycerol feed contains less than about 12% water by weight.

Also disclosed is a system for converting glycerol to propylene glycol. The system includes a reactor containing a

2

catalyst for facilitating the conversion of glycerol into propylene glycol. The system also includes a glycerol feed stream that has been primarily diluted with propylene glycol rather than water in order to facilitate the reaction chemistry and the catalytic conversion of the glycerol to propylene glycol. Also disclosed as part of the system is a recycle stream whereby the reaction product, or a portion of the reaction product, is fed back to dilute the glycerol feed stream.

In certain embodiments, the diluted glycerol feed comprises from about 40% to 60% by weight propylene glycol. In another aspect, the diluted glycerol feed comprises from about 40% to 60% by weight glycerol. In certain disclosed embodiments, the reaction is carried out at a temperature from about  $160^{\circ}$  C. to about  $240^{\circ}$  C., and at pressures from about 400 to about 1600 psi.

The foregoing and other objects, features, and advantages of the processes and systems disclosed herein will become more apparent from the following detailed description.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagram illustrating the use of reactor effluent as the primary solvent instead of water.

#### DETAILED DESCRIPTION

Glycerol that has been generated from the biodiesel process is mostly free of water after the final methanol recovery step, yet its catalytic upgrading to propylene glycol requires up to 60% solvent by weight to enable the reaction chemistry. This is particularly troublesome since the water must be subsequently removed in immediate and costly downstream separations. The elimination of water as a solvent would provide a more efficient and resourceful process, and would provide cost savings on both reactor operations and separations.

As illustrated in FIG. 1, an alternate reactor configuration was proposed using reactor effluent as the primary reactor solvent instead of water. In this embodiment, an internal recycle of nearly 60% was proposed. Although the amount of the product stream proposed to be recycled is quite large, it was anticipated that this process could yield certain advantages when compared to the baseline process.

Specifically, the water load to separations would be reduced by about 90%, and overall product sent to separations would be reduced by more than half while still maintaining the same rate of propylene glycol output. The reactor size would remain nearly the same. The recycled solvent would come in near reaction temperature, thereby reducing the need for added energy requirements. The base and some glycerol are also partially recycled in the system, thereby resulting in a more resourceful and efficient process.

It was also anticipated that the process could suffer from several disadvantages. Specifically, stability of propylene glycol becomes a crucial factor and any consumption of propylene glycol would have a magnified effect on the true process yield. Also, byproduct recycle could lead to unwanted effects on the primary chemistry, and possibly produce a more recalcitrant byproduct in the separation processes. In addition, propylene glycol as a solvent could affect the catalytic chemistry, including diffusion limitations or reduced hydrogen access to the catalyst.

The disclosed embodiments address the issues that have arisen as a result of the use of biodiesel derived glycerol and the need for the addition and immediate subsequent removal of water primarily around the catalysis unit operation. In particular, disclosed are processes and systems wherein reac-